

REPORT

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THE SYNTHESIS OF MONOMERS WITH PENDENT ETHYNYL GROUP FOR MODIFIED
HIGH PERFORMANCE THERMOPLASTICS

NASA GRANT: NAG - 1 - 905

N92-33619

Unclass

G3/23 0118166

FOR THE PERIOD: September 1988 to August 31, 1992

by

Godson C. Nwokogu, Miquel D. Antoine and Omari Ansong
Department of Chemistry
Hampton University
Hampton, Virginia 23668

(NASA-CR-190821) THE SYNTHESIS OF
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THERMOPLASTICS Report, Sep. 1988 -
31 Aug. 1992 (Hampton Univ.) 19 p

September 1992

A. INTRODUCTION

The objectives of this project, which was started in September 1988, were to develop synthetic schemes for the following classes of modified monomers: (1) difunctional triarylethanes with pendent acetylenic groups and (2) tertiary aspartimides with terminal acetylene groups at the two ends. Our efforts have resulted in the successful development of high yield schemes for the syntheses of several diamino- and bisphenolic analogs of difunctional triarylethanes with pendent ethynyl group. A scheme for one new tertiary aspartimide has also been established. Multi-gram samples of all prepared new monomers have been provided to our technical contact at NASA-LaRC and preliminary polymerization studies have been encouraging. Details of the accomplished work within the last four years are described here. It should be noted that this project has been funded for three out of the four years but we have maintained continuous activity on the project through funding from the National Science Foundation. Interim reports were submitted every six months for the first year and a half of this project. Progress reports have been included in all renewal applications.

B. RESULTS AND DISCUSSION

In 1988, we started this project on polymer optimization involving the development of synthetic schemes for difunctional condensation monomers bearing pendent ethynyl groups as the reactive functions for cross-linking of the resulting linear

condensation polymers. The initially targeted monomers were the diamino- and bisphenolic triarylethanes **1** — **4**, **11** and **17**, the acetylene-capped tertiary aspartimide **5** and a group of acetylene - containing terminators for prepolymers represented by the benzil **6**(Table I).

Table I

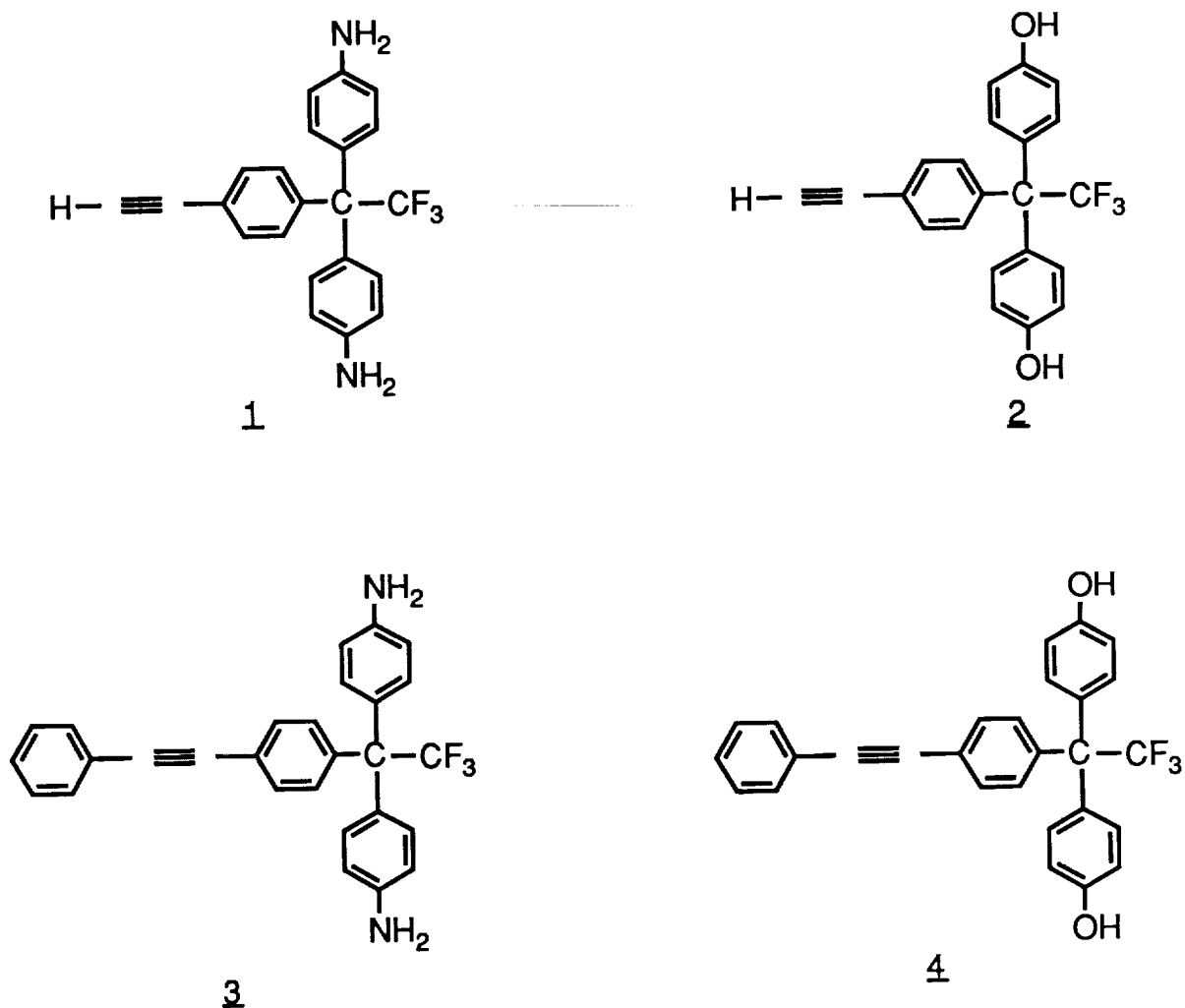
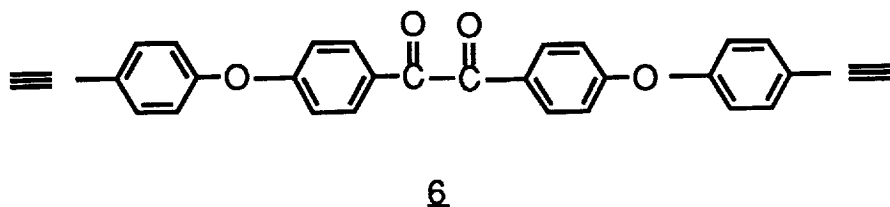
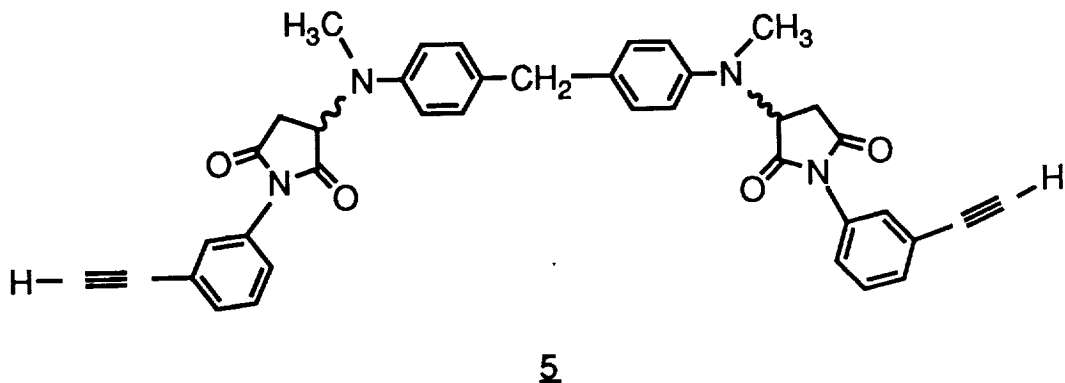


Table I Cont'd



B.1. The Synthesis of Bisamino-Analogs of Triarylethanes with Pendent Ethynyl Group.

At the beginning of this project, it was not known whether the acetylenic function on monomers such as 1 — 4(Table I) would survive the usual condensation polymerization reaction temperature of ~155°C. An early resolution of this uncertainty about the survivability of the ethynyl functional group was necessary in order to determine the usefulness of the compounds proposed to be synthesized. Because of the greater reactivity of terminal acetylenes towards addition as compared with internal ethynes, our efforts, initially, were directed towards the preparation of the structurally

simpler but synthetically more difficult monomers **1** and **2**. If these more reactive acetylenes survived the initial condensation polymerization process, then the other non-terminal analogs would also be stable.

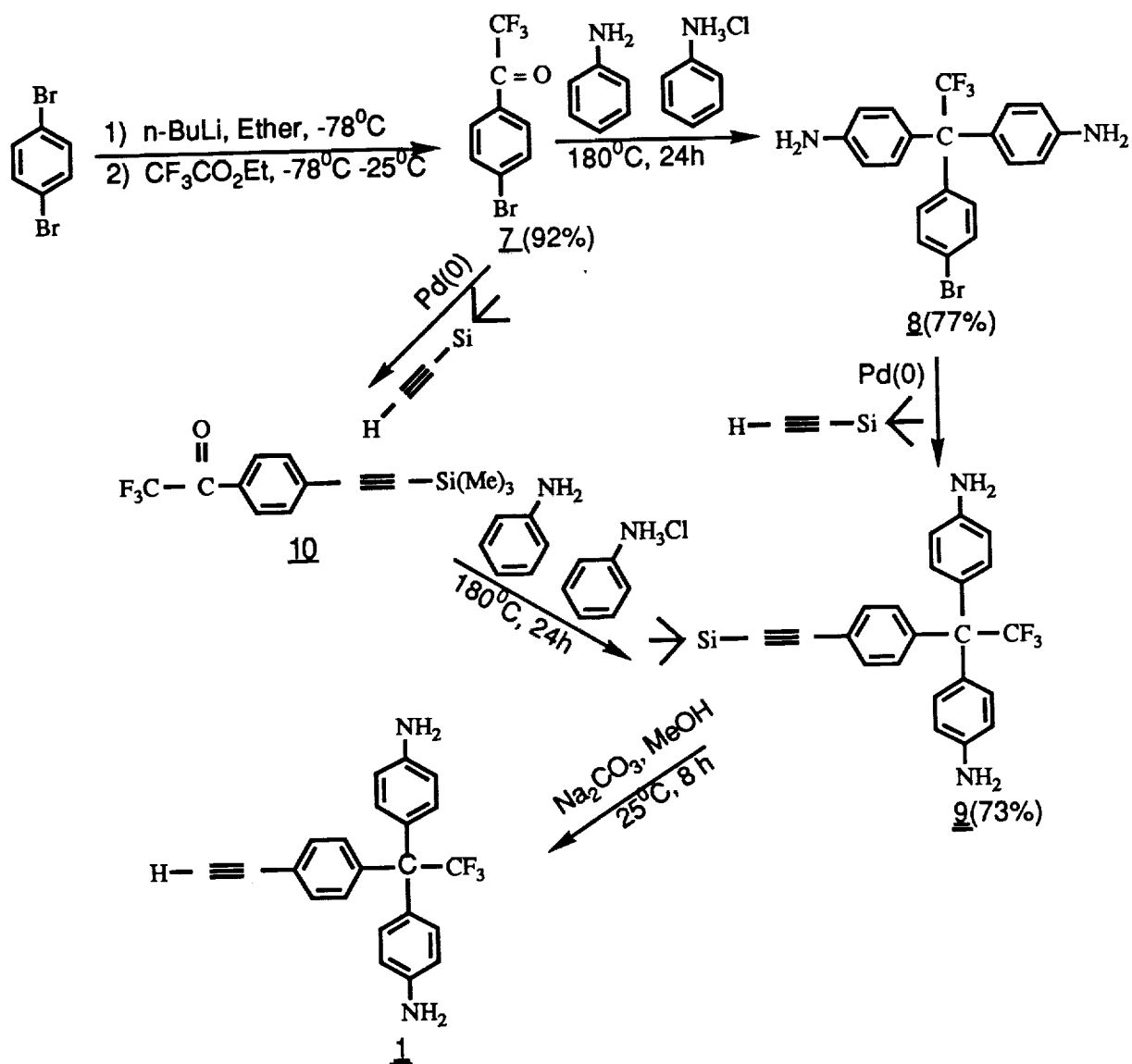
We have successfully developed and optimized a synthetic scheme for the compound **1** and preliminary polymerization studies show that the pendent ethynyl group does survive the conditions of polymerization. The resulting polymers also do cross-link on curing of the fabricated materials. With the usefulness of the ethynyl group for cross-linking of polymers formed by condensation reaction established, it was then certain that the other monomers projected for synthesis by us would be relevant to and useful in the studies to improve the properties of such engineering thermoplastics through ethynyl-based cross-linking.

B.1.1. Synthesis of 1,1-Bis(4-aminophenyl)-1-(4-ethynylphenyl)-2,2,2-trifluoroethane**1**

We have investigated the synthesis of **1** by two routes as shown in Scheme I, each of which begins with the bromoketone **7**. We have optimized the yield of the bromoketone **7** to 92% in scaled-up reactions without having to use reverse addition technique.

One of the routes in Scheme I involves condensation of **7** with aniline by the method of Kray² to yield the diaminobromide **8** which would then undergo palladium(0)-catalyzed ethynylation with trimethylsilylacetylene(TMSA) to give the adduct **9**. Prodesilylation of **9** would lead to the target compound **1**.

Scheme 1



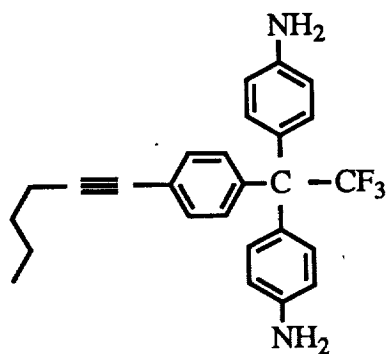
The diaminobromide **8** was obtained in 77% yield. Efforts to drive the Pd(0)-catalyzed ethynylation of the diaminobromide **8** with TMSA to completion in triethylamine with less than 5 mol% of catalyst and CuI as co-catalyst were unsuccessful. Because all efforts to remove the unreacted diaminobromide from the coupled product **9** proved futile, it was necessary to find a condition that would lead to

complete conversion of the bromide **8**. This condition was found to be the use of a 3:1 vol/vol mixture of triethylamine and N-methylpyrrolidine. A yield of 73% of **9** was obtained by using this solvent mixture with 5 mol% each of Pd(0)-catalyst and CuI. Protodesilylation of crude **9** gave, in a scaled-up reaction, 79% of **1**.

The alternative route to the monomer **1** (see Scheme I) was undertaken to determine the optimal order for the two major reactions in the scheme - condensation and Pd(0)-catalyzed ethynylation. Pd(0)-catalyzed coupling of the bromoketone **7** was anticipated to be more facile than that of the diaminobromide **8** due to the activating effect of the carbonyl group. This was borne out by the fact that **7** was ethynylated completely with TMSA in triethylamine without the use of CuI as co-catalyst. Attempted Kray condensation of **10** with aniline gave a solid product which was not the expected **9** (from ^1H NMR and mass spectrum).

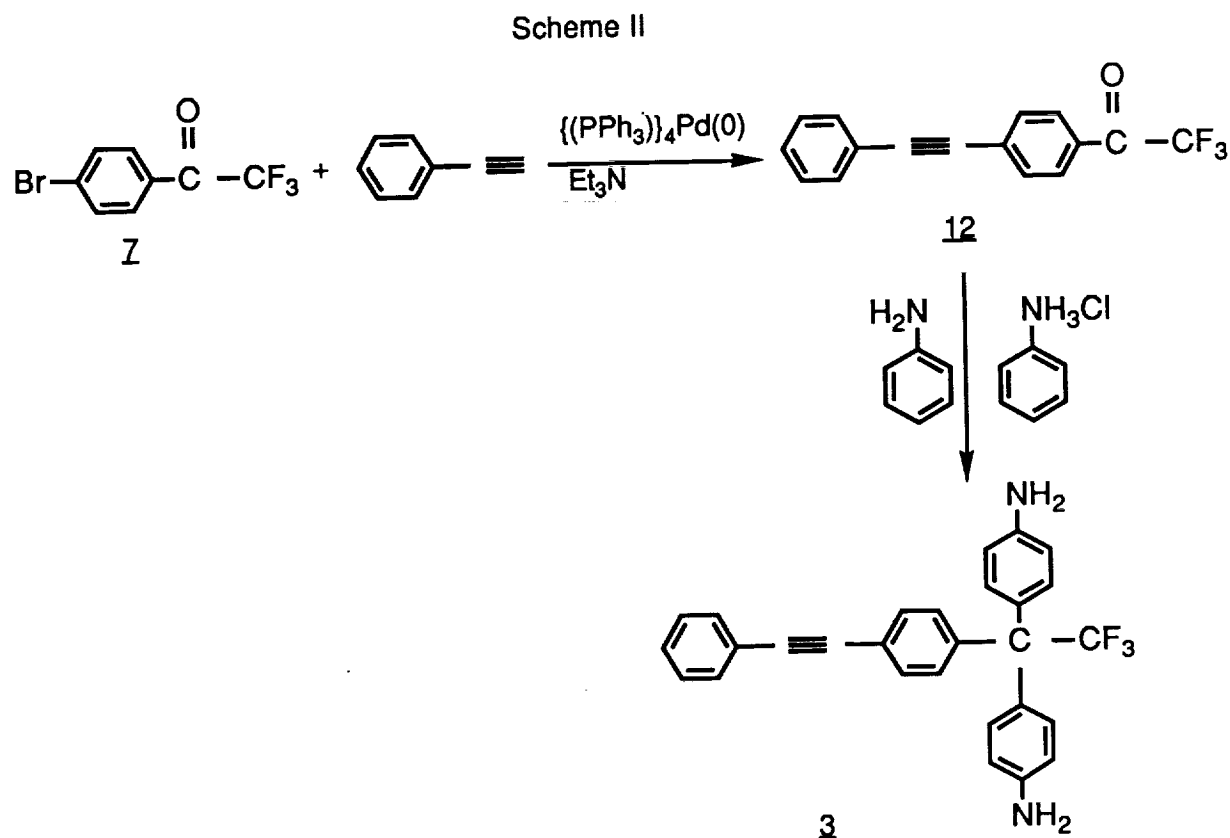
B.1.2. Synthesis of Other Diaminotriarylethanes with Pendent Ethynyl Group (3 & 11).

The above optimized reaction condition for the ethynylation of **8** was applied to its coupling with phenylacetylene to give the monomer **3** in 61% and with 1-hexyne to give **11** in 76% yield.



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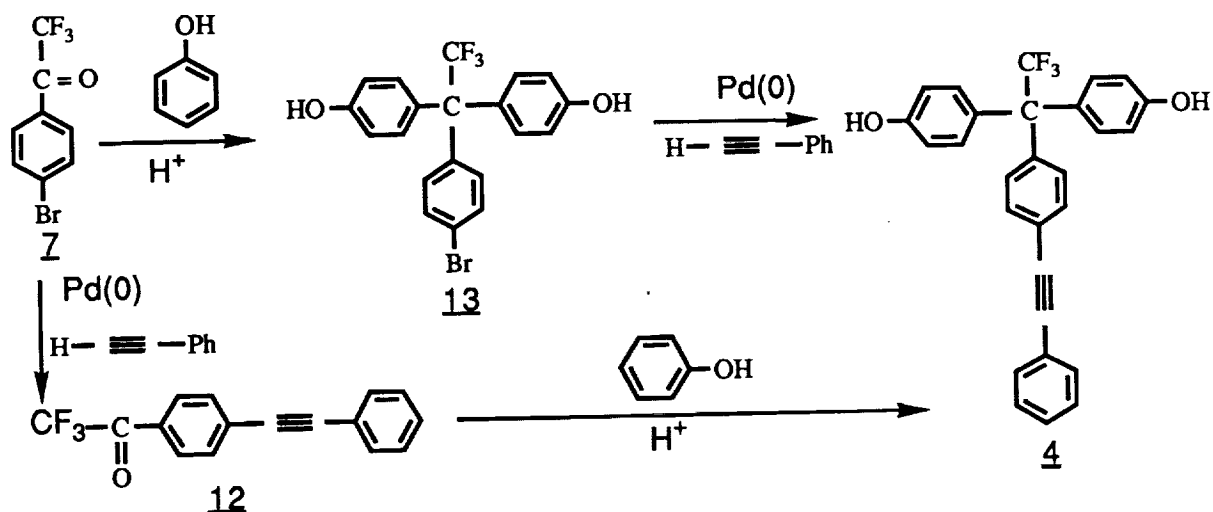
The alternative route to the ethynylated monomers, which was not successful for the preparation of **1** was, however, successful with (phenylethynyl)trifluoromethylacetophenone **12**(Scheme II).



B.2. Synthesis of 1,1-Bis(4-hydroxyphenyl)-1-(4-ethynylphenyl)-2,2,2-trifluoroethane **2** and Analogs **4** & **17**.

For this class of monomers, we also examined two alternative routes, as illustrated in Scheme III with **4**.

Scheme III

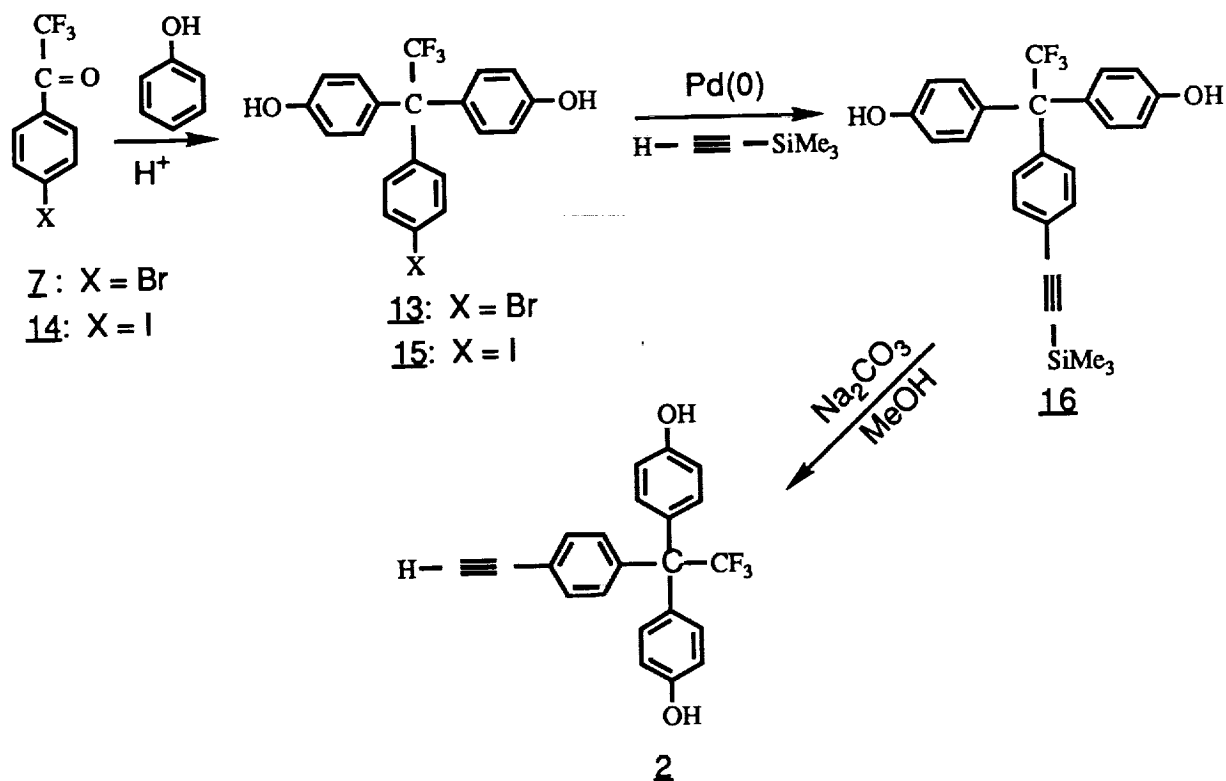


B.2.1 Synthesis of 1,1-Bis(4-hydroxyphenyl)-1-(4-ethynylphenyl)-2,2,2-trifluoroethane

2.

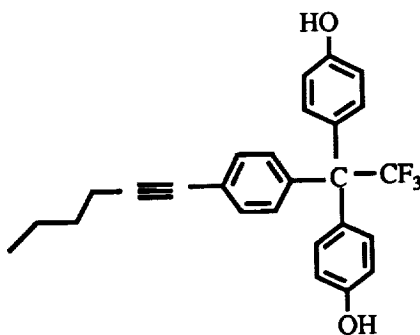
The synthetic scheme for 2 is given in Scheme IV. Condensation of the bromoketone Z with phenol using 2 - 6 mol% of triflic acid gave the bisphenol bromide 13 in 80% yield. With the iodoketone 14 the yield of the corresponding bisphenol iodide 15 was 77%. The bisphenol bromide was found to be more reactive than the diamino-analog as demonstrated by the fact that it's Pd(0)-catalyzed ethynylation with TMSA in triethylamine occurred with complete conversion of the bromide. The amount of Pd(0)-catalyst and CuI used was 4 mol% and the yield of the protodesilylated product 2 was 73%. The alternative route was not tried in the preparation of this compound.

Scheme IV



B.2.2 Synthesis of the Analogs **4** and **17**:

The hexynyl coupling adduct **17** was prepared also in 73% yield by the same conditions used to prepare the trimethylsilyl adduct **16**. This condition and its other variations could not lead to complete conversion when the bromide **13** was coupled with phenylacetylene in attempts to prepare **4**. In order to overcome this difficulty, the iodide **15** was used instead. The $\text{Pd}(0)$ -catalyzed coupling of the iodide **15** with phenylacetylene occurred with complete conversion of the iodide to give 82% of **4** using 4 mol% of Pd -catalyst and CuI in Et_3N .



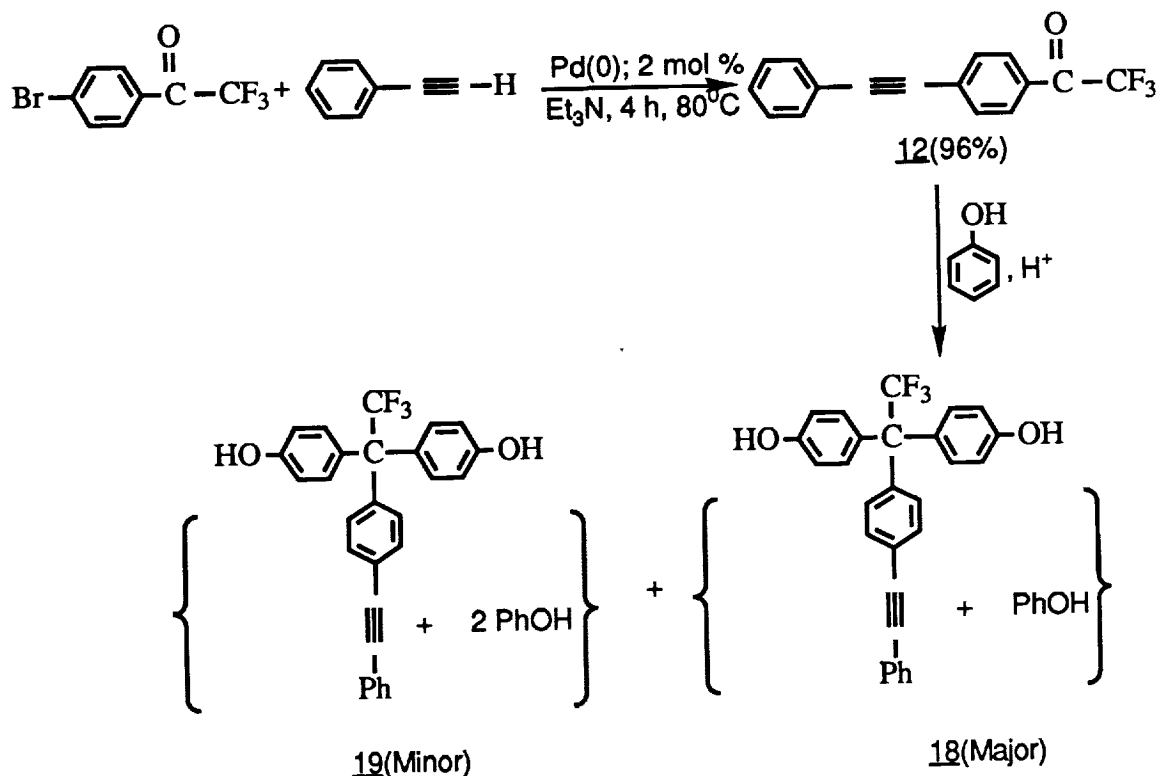
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The alternative route involving ethynylation of the bromoketone 7 followed by condensation with phenol was attempted with phenylacetylene as shown in Scheme V. Even though the condensation occurred at the carbonyl carbon, the initially formed product presumably suffered the addition of one and two molecules of phenol across the triple bond to give the adducts 18 and 19. The exact structure of the addition across the triple bond has not yet been established.

B.3. Acetylene-capped Tertiary Aspartimides

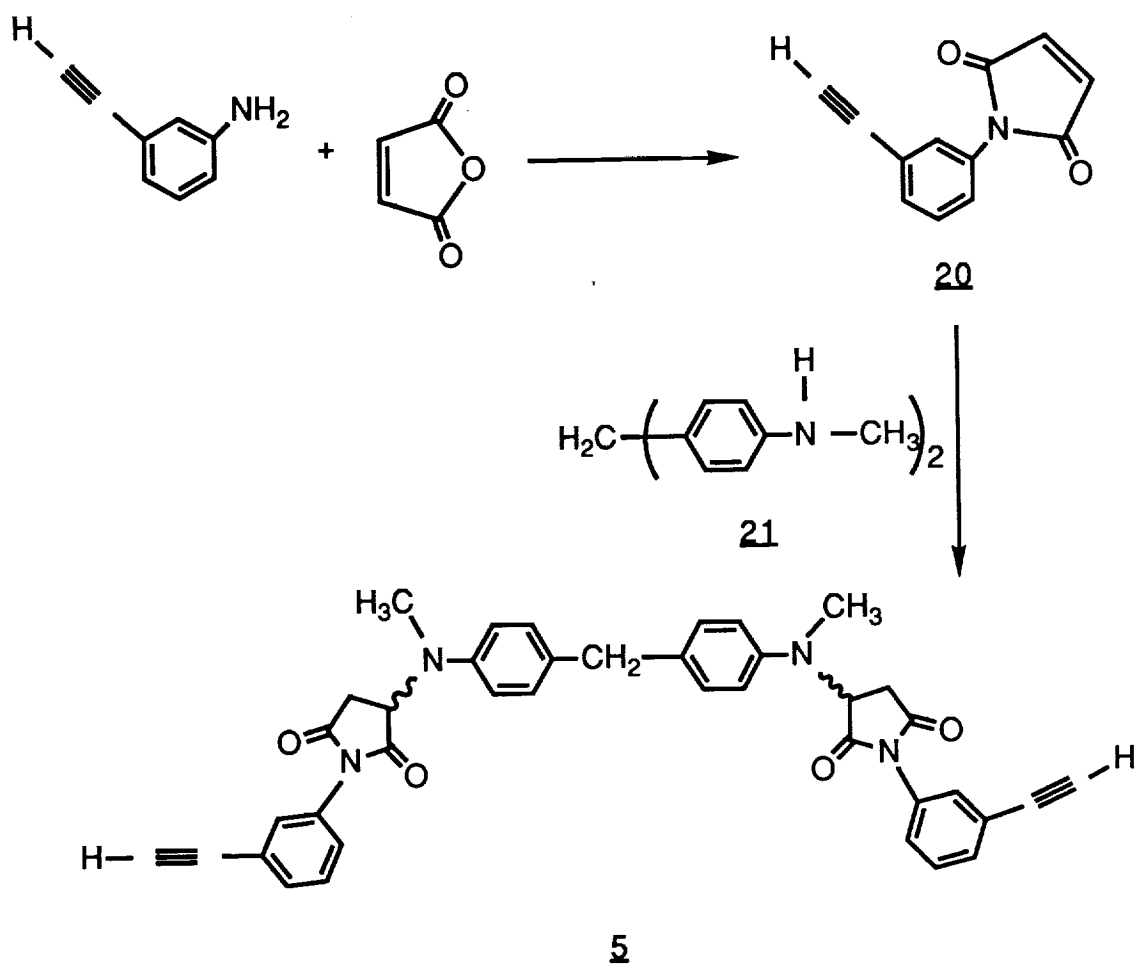
The preparation of samples of the tertiary aspartimide 5 followed a reported sequence for secondary acetylene-capped aspartimides³ as illustrated in Scheme VI.

Scheme V



The maleimide **20** was obtained in 69% yield using N,N-dimethylformamide as solvent. Attempted condensation of this maleimide with the diamine **21** in refluxing glacial acetic acid resulted in a discolored solid and a low mass balance for the reaction. Repeating the reaction at room temperature, however, resulted in a yellow suspension which was isolated by pouring in water. The mass balance for the reactions run this way varied from 91 - 100%. This material was identified to be **5**.

Scheme VI

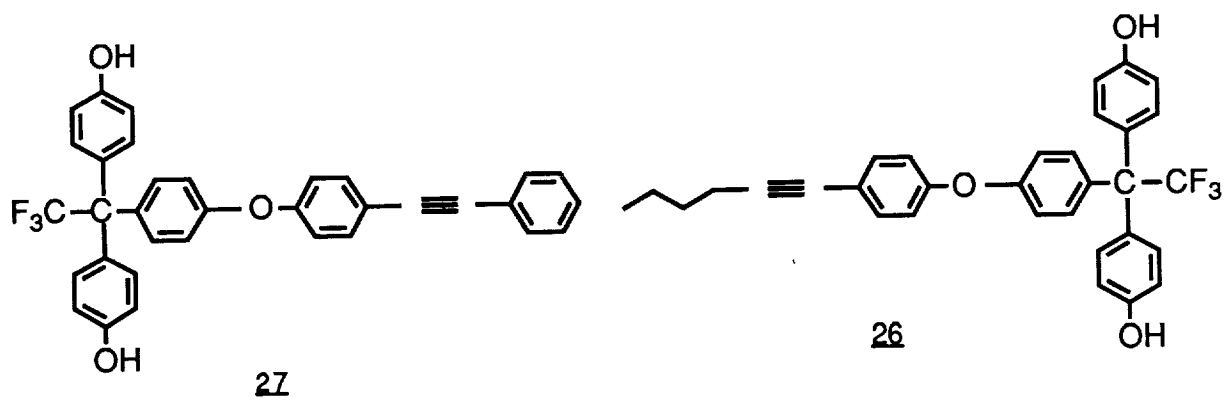
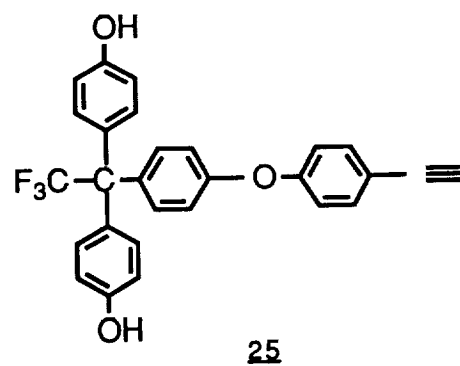
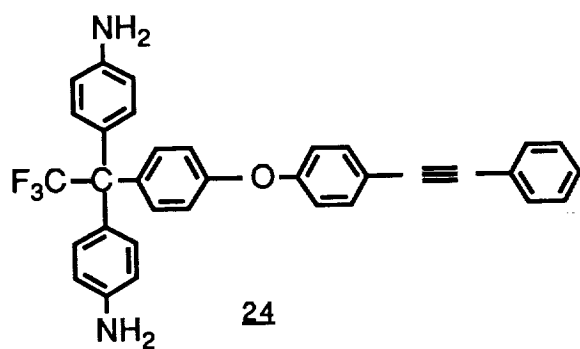
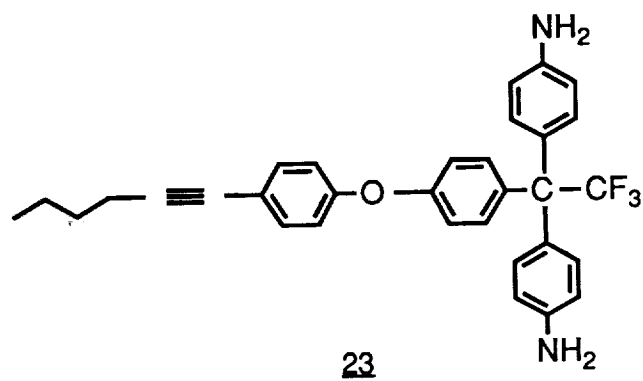
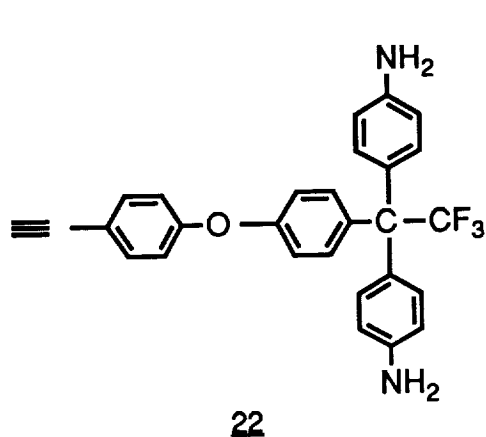


B. 4. Phenoxy-analogs of Triarylethanes with Pendent Ethynyl Groups

Having completed the synthesis of compounds 1, 2, 3, 4, 5, 11, and 13, and 17, and because of the encouraging preliminary data on their polymerization and cross-linking ability by NASA-LaRC polymer scientists, we turned our attention to the

development of synthetic schemes for the phenoxy- analogs **22** - **27**(Table II).

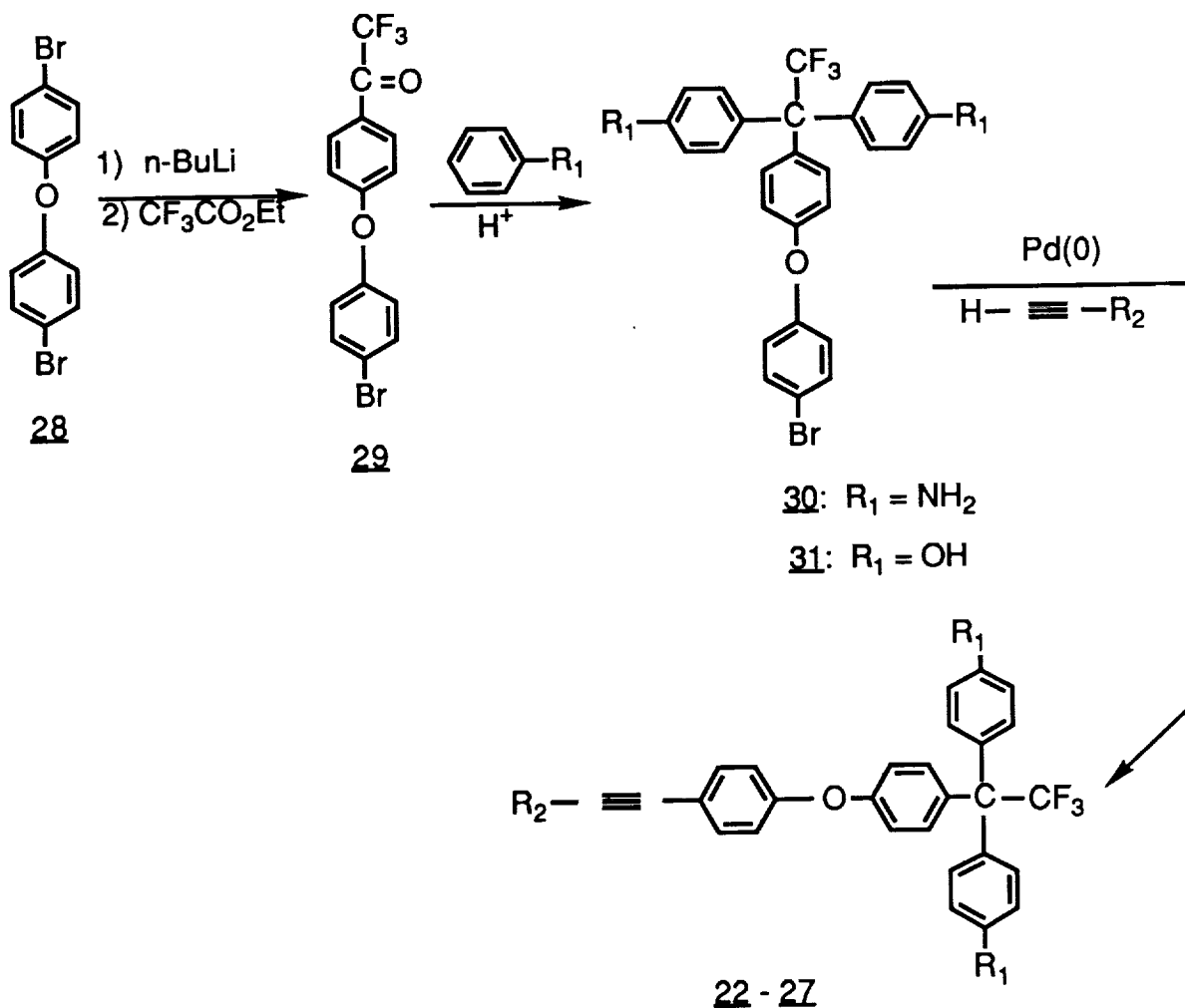
Table II



The strategy for the synthesis of the diamino-compounds 22 - 24 and the bisphenol analogs 25 - 27 were expected to be similar to those used for the synthesis of 1 - 4(Table I), 11 and 17 . The scheme for the condensation/coupling sequence is given in Scheme VII.

Results from our efforts to prepare the bromoketone 29 showed that unlike the reaction for the preparation of the bromoketone 7(Scheme I), the dibromide 28 does not undergo metal-halogen exchange at -78°C . We have been able to obtain some of the ketone 29 by running the metal-halogen exchange at temperatures higher than -78°C . These investigations also showed that unlike the dibromo- and diiodo-benzene for which only mono-metallation occurred no matter how much excess n-BuLi was used(up to 300% excess), excess n-BuLi in the reaction with 28 leads to products different from the desired 29. We have determined that the keto-bromide 29 can be prepared in XX% yield if the metal-halogen exchange occurred at -40°C with about 5% excess of n-BuLi and the trapping of the aryllithium with ethyl trifluoroacetate at -78°C .

Scheme VII



22: $\text{R}_1 = \text{NH}_2$, $\text{R}_2 = \text{H}$; 23: $\text{R}_1 = \text{NH}_2$, $\text{R}_2 = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$; 24: $\text{R}_1 = \text{NH}_2$, $\text{R}_2 = \text{C}_6\text{H}_5$

25: $\text{R}_1 = \text{OH}$, $\text{R}_2 = \text{H}$; 26: $\text{R}_1 = \text{OH}$, $\text{R}_2 = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$; 27: $\text{R}_1 = \text{OH}$, $\text{R}_2 = \text{C}_6\text{H}_5$

Acid-catalyzed condensation of the bromoketone 29 with aniline gave 70% of the diamine 30 whereas the use of phenol led to 94% of the bisphenol-bromide 31. So far, we have completed the ethynylation of the bromodiamine 30 with phenylacetylene to obtain the ethynylated diamine 24(75%) and have submitted 10g of this material for

polymerization studies.

C. SUMMARY OF TECHNICAL REPORT

We have developed the synthesis of the compounds 1, 2, 3, 4, 5, 11, 13, 17, 24 and 8 and supplied from 10 - 20g of each of these new materials to our technical contact at NASA Langley Research Center for polymerization studies. Two presentations have been made on the polymerization studies of the diamino-monomers by NASA-LaRC polymer scientists and two presentations have resulted from the synthesis of the monomers 1 - 4, 11 and 17 by our group.

We are currently working on developing and optimizing schemes for the synthesis of the remaining diaminophenoxyphenyl analogs 22 and 23 and the three bisphenolic analogs 25 - 27. A paper detailing the chemistry of these syntheses will be prepared when the schemes for these remaining compounds have established and optimized.

D. Personnel

This project, since the 1988/89 academic year, has provided partial support for two graduate students whose M.S. thesis research work were based on the project:

1. Ms. Miquel D. Antoine obtained her M.S. degree in the Spring of 1991 and has

already completed, by the time of her MS thesis defence here, her first year in the PhD program at Emory University, Atlanta.

2. Mr. Omari Ansong completed his M.S. degree requirements in the Spring of 1991. He is a resident alien. He worked, until Fall 1991, at the R & D Department of Hoechst Celanese in Providence, Rhode Island. He started a PhD program in polymer chemistry at Rensselaer Polytechnic Institute in the spring of 1992.
3. An undergraduate junior, Ms. Melanda Colson, was selected to receive the NASA scholarship included in our 1990/91 grant. She received tuition and stipend for the Fall and Spring semesters of the 1991/92 academic year.

E. Professional Contributions

Results from the synthesis of the monomers have been presented in December 1990 at the combined Southeast/Southwest regional meeting of the ACS in New Orleans, Louisiana and in April, 1991 in Washington, DC at the 18th annual national conference of the National Organization for the Professional Advancement of Black Chemists and Chemical Engineers (NOBCChE). Results on polymerization studies of these monomers were presented by NASA-LaRC personnel at the San Francisco national meeting of the ACS in April, 1992. Abstracts of the presentations are enclosed.

F. ACKNOWLEDGEMENTS

This project is also partially supported by the National Science Foundation, Grant # RII-8912609.

G. REFERENCES

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3. Hergenrother, P.M., Havens, S.J., Connell, J.W., Polym. Prepr. 27(2) 408, 1986.